FIRST QUARTERLY REPORT

STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION OF THE ALKALINE SILVER ELECTRODE

JPL 951911

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

E. A. Butler

A. U. Blackham

Chemistry Department

Brigham Young University

Provo, Utah 84601

August 15, 1967

ABSTRACT

A method for obtaining data for a polarization curve of the silver anode in an ammoniacal electrolyte has been tested. The principal advantage of the method is that it eliminates ohmic overpotential from the measurement and does not introduce the problem of capillary shielding.

Further testing of the method for determination of the effective electrolytic surface area of sintered silver electrodes is being carried out through the development of control sintered electrodes and through application of other methods of surface area determination.

Apparatus is being set up to investigate the effects of ultrasonic vibrations on charging capacity, electrolyte depletion, and surface smoothing.

SECTION I

POTENTIAL AND CURRENT VARIATIONS OVER THE ELECTRODE SURFACE (POLARIZATION MEASUREMENTS)

Data were presented in the Final Report[1] of JPL Contract 951554 which showed quantitatively current and potential distributions around working electrodes. The main objective of these studies was to find the effect of electrode and cell geometry on current and potential distribution. Preliminary studies of the relationship of current density, conductivity, and temperature to the current and potential distribution have now been made. A polarization curve of the silver electrode is needed before these variables can be adequately investigated. It was pointed out in the Final Report[1] of JPL Contract 951554 that a polarization curve is necessary before our current distribution data can be compared with Wagner's[2] theoretical analysis of current distribution.

Polarization data can also be used for surface area determinations. The method is based on the principle that polarization is a function of current density and thus of surface area. Wranglen and Warg determined the surface area of nickel samples from measurements of hydrogen overvoltage (polarization) at several current densitites[3]. Plots of their data are shown in Figure 1. The Tafel equation for the overpotential η, of an electrode with an area, A, through which a current, I, is flowing is:

$$\eta = a + b \log (I/A) = a + b \log I - b \log A$$

where a and b are constants. If η is plotted as a function of I for two electrodes which are identical except for area then two parallel lines result as shown in Figure 1. The difference in η between these lines determines the ratio of the two surface areas by the relation $\log (A_2/A_1) = (\eta_1 - \eta_2)/b$. The slope of the Tafel lines is b.

Apparatus and Reagents

The modified Haring cell and Luggin capillary measuring system has been described[1]. The cell enclosure was sealed so that significant loss of ammonia gas from the electrolyte occurred only when the enclosure was necessarily open, e. g. for adding or changing electrolyte. A water jacket was built into the walls and bottom of the Haring cell. Water from a constant temperature bath was circulated through this jacket to maintain a temperature of $20.0 \pm 0.1^{\circ}C$. For runs made with current densities less than 1 ma/cm^2 the temperature control was $\pm 0.04^{\circ}C$. The smaller heating effect of lower currents on the cell electrolyte permitted this better control.

Three different electrolytes were tested. All chemicals used were reagent grade.

Electrolyte A	Electrolyte B	Electrolyte C
14.7 $\underline{N}$ NH_4OH	14.7 $\underline{N}$ NH_4OH	14.7 $\underline{N}$ NH_4OH
0.025 $\underline{N}$ $AgNO_3$	0.025 $\underline{N}$ $AgNO_3$	0.10 $\underline{N}$ $AgNO_3$
0.10 $\underline{N}$ KNO_3	0.05 $\underline{N}$ KNO_3	0.10 $\underline{N}$ KNO_3

The test anodes were silver foil 99.9+ % pure. The cell cathode was platinum foil which soon became plated with silver. No measurements were made until the cathode was covered with silver plate.

Polarization Curve Experiments

The purpose of these experiments was to establish a polarization curve for a silver anode in an ammoniacal electrolyte (Electrolyte A, above). We chose to use a Luggin capillary system for making the measurements. The problems encountered in the direct measurement of overpotential with a Luggin capillary are discussed below.

Concentration Overpotential. The change in electrode potential caused by the accumulation of reaction products or the depletion of

reactants can be decreased to a small value by vigorous agitation of the solution and by use of high initial concentrations of the ions involved in the electrode reaction (in this case silver-ammine complex ions). We are using both of these devices to reduce the concentration overpotential in the polarization measurements. The concentration overpotential, $\eta_{conc.}$, at any current density, i, is represented in its simplest form[4] by:

$$\eta_{conc.} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_L}\right)$$

where i_L is the limiting diffusion current density and R, T, n, and F have their usual significance. We have determined experimentally that the limiting current density for the silver anode in Electrolyte A is greater than 77 ma/cm^2. If we assume 77 ma/cm^2 to be our limiting current density then $\eta_{conc.}$ is 0.3 mv at 1 ma/cm^2 and is 1.0 mv at 3 ma/cm^2. This shows that $\eta_{conc.}$ for our polarization measurements is small at current densities lower than 3 ma/cm^2 which is the range of current densities of interest.

Current Distribution. Because polarization is a function of current density, the preferred electrode would have a uniform current distribution; hence the local current density would equal the average current density. If this is not the case the current distribution will change as the average current density changes. This causes a corresponding shift in the ratio of local current density to average current density at any one point. For this reason the Haring cell which has a uniform current distribution[1, 5] was chosen for the polarization measurements.

Impurities. There are several ways in which impurities can produce errors in overpotential measurements[6]. These effects include: (a) prolonged potential drift with time, (b) irreproducibility of overpotential measurements for any given current density, and (c) potential changes which accompany changes in stirring rate, particularly at low current densities.

IR-drop and Capillary Shielding. In any potential measurement made of a working electrode using the direct method an ohmic potential

drop will be present which is proportional to the distance between the capillary tip and the electrode surface. A number of methods have been used to eliminate IR-drop from overpotential measurements. Null methods such as the Pearson bridge[7] or similar methods[8] which use alternating current to determine the resistance of the solution have been used. Electronic commutator interrupter circuits which eliminate IR-drop from potential measurements have been designed. Stern and Geary[9] have derived an equation which relates the slope of the linear region of a polarization curve (at very small overvoltages) to the corrosion rate and Tafel slopes. This equation is useful because a polarization curve can be made from overpotential measurements at very small currents (less than a few microamperes) where IR-drop effects are small. It is a common procedure to place the measuring capillary as close as possible to the electrode surface to eliminate IR-drop. The potentials measured with a capillary close to the electrode surface are, however, different from the true potential because of capillary shielding[10].

The micrometer drive in our apparatus makes possible a series of potential measurements with the capillary placed at various known distances from the electrode surface. These measurements can be extrapolated to the potential at the electrode surface because of the linear relationship between IR-drop and distance. The data for Figure 2 were taken in this manner. To test this method, similar measurements were made using the three electrolytes A, B, and C (page 2). The results are compared in Figure 3. As expected, the slopes of the three plots are different because of the different conductivities of the three electrolytes, but all three lines converge to a common intercept. This indicates that the ohmic overpotential can be eliminated from overpotential measurements leaving only the activation overpotential. Another advantage of this method is that the capillary need not be brought close enough to the electrode surface to cause significant shielding. There are data points in Figure 2 taken at distances closer than 0.05 inch which show the effect of shielding by the capillary. This is in agreement with

Barnartt's measurements[10] which predict that significant shielding would occur 0.04 inch from the electrode surface for the system used here. Similar measurements at several current densities are now underway which will provide data for a polarization curve.

Future Work

1. We plan to finish work on the polarization curve of the silver anode in the ammoniacal electrolyte.
   a. This curve will be used as a basis for surface area measurements of sintered silver electrodes.
   b. This curve will be used to compare our current distribution data with Wagner's[2] theory and to evaluate the effect of other variables including temperature, electrolyte conductivity, and average current density on the current distribution.

SECTION II

DETERMINATION OF EFFECTIVE ELECTROLYTIC SURFACE AREA

Two approaches are being used to test further the method described in the Final Report[1] of JPL 951554 for the determination of the effective electrolytic surface area of sintered silver electrodes in alkaline solution.

The first approach involves the preparation of a control sintered electrode. This electrode is made from silver powder of known particle size and shape. From the size, shape, and weight of powder used in a given electrode the total surface area of the powder can be calculated. This powder is then pressed around a grid of silver metal in a die into an electrode, and sintered at 1000°F for one-half hour. If the powder used in the preparation of the electrodes were made up of spherical particles of known diameter, then calculations show that the surface area of the powder decreases with increase of particle size. Of course, the surface area of the powder making up the electrode will be changed by pressing and sintering. If the pressure used in the formation of the electrode and the weight of powder used are kept constant and of the surface area of the powder is changed by varying the particle size, it is hoped that effective surface area of the electrode will also be changed as a function of the variation of particle size. We have made control electrodes from powder which we screened to a known range of particle sizes. The measured surface areas of these electrodes followed the expected trend with change in particle size. As indicated in Table 1, the surface area drops from 250 cm^2/g to 100 cm^2/g as the average diameter of the silver particles increases from 0.05 mm to 0.08 mm. These screened particles were found upon microscopic examination to be of such irregular shape that they did not lend themselves to a calculation of surface area per particle, and thus no quantitative relationships between changes in particle size and effective surface area were established (see Figure 4). Work is now underway to obtain silver powder made up

from particles which are spherical in shape and of known diameter.

The pressures used in the formation of these control electrodes, along with the weight of powder, affect the electrolytic surface area to a great extent. Pressures of the order of two thousand pounds per square inch produce surface areas one third of those measured in electrodes formed at pressures of the order of thirty pounds per square inch. With better information on the total surface area before pressing and sintering the effects of pressure and weight upon the effective electrolytic surface area can be determined.

The second approach involves finding other methods in the literature which might be used to determine electrolytic surface area and comparing the results of these measurements on our sintered silver electrodes with the results obtained by our method. Only one method has been found that both uses an electrochemical reaction as a basis for its surface area determination and is suitable for sintered electrodes. This involves the use of polarization curves and is now being tested in conjunction with the work described in Section I of this report[3]. Another method using an electrochemical basis for its determination of surface area is that of double layer capacitance; however, methods have not yet been found to extend this determination to sintered electrodes because of the roughness of these electrodes. Several gas adsorption methods have been used to determine surface areas of metal powders and porous materials. These do not hold the same interest because they are not based upon an electrical measurement as are the above mentioned methods.

SECTION III

THE EFFECTS OF ULTRASONIC VIBRATIONS ON THE OXIDATION OF SILVER

The depth of oxidation of a smooth silver electrode is a function of the current density[11]. This observation is the basis for a determination of effective electrolytic surface area[1]. Of concern now is the nature of other factors which will influence the depth of oxidation such as ultrasonic vibrations. Our studies will be concerned with the effects of ultrasonics on charging capacity, electrolyte depletion, and surface smoothing.

Charging Capacity. Skalozubov, Kukoz, and Mikhailenko observed a 10% increase in the depth of oxidation (charging capacity) of sintered silver electrodes which were subjected to ultrasonic vibrations during the intial oxidation[12]. This increase was retained through subsequent cycling without further ultrasonic treatment.

Ultrasonic vibrators are often used to clean delicate instruments because the vibrations agitate the cleaning solution into the minute cracks, pores, and openings. This suggests the use of ultrasonics to circulate electrolyte into the cracks and pores of the sintered electrode. This agitation may expose pores and surfaces to the electrolyte which are not otherwise wetted and thus may account for the permanent 10% increase found by Skalozubov, et al[12].

Electrolyte Depletion. Circulation of electrolyte through the pores of the sintered electrode may also show whether the oxidation is limited by a depletion of the electrolyte in the small pores of the electrode.

Surface Smoothing. An X-ray diffraction study by Wales and Burbank shows that the surface of a silver electrode is smoothed by cycling the electrode at low current densities[13]. An explanation may be that the silver ions move from a silver lattice point to a silver oxide lattice point during oxidation and return to a silver lattice structure during reduction[14]. Slow reduction (low current density) allows a more uniform deposition of

silver into the silver lattice. If external vibrations allow the ions to move more freely through the lattice, surface smoothing may also be obtained by cycling the electrodes with vibrations. We will investigate this by comparing surface areas of electrodes cycled with ultrasonic vibrations with surface areas of electrodes cycled without vibrations.

Apparatus. Our studies of these effects of vibrations on oxidation of silver will require smooth silver electrodes as well as the commercial sintered electrodes. Our smooth electrodes will be prepared by vacuum depositing silver on glass substrates similar to those used for surface area determination. For this purpose we are constructing a high vacuum system with a larger capacity and a higher ultimate vacuum than was previously available to us. We are also setting up ultrasonic vibrators of various frequencies and amplitudes for use in these studies. The details of this experimental set-up will be given in the next report.

TABLE 1

	Particle mesh size of powder used in forming of electrode	Average diameter of particles (mm)	Weight of electrode (gm)	Effective electrolytic surface area of electrode (cm^2)	Area per weight (cm^2/gm)
(1)	270> P> 325	.048	.1402	35.8	250
(2)	250> P> 270	.055	.1924	33.6	170
(3)	140> P> 170	.079	.2700	28.2	100

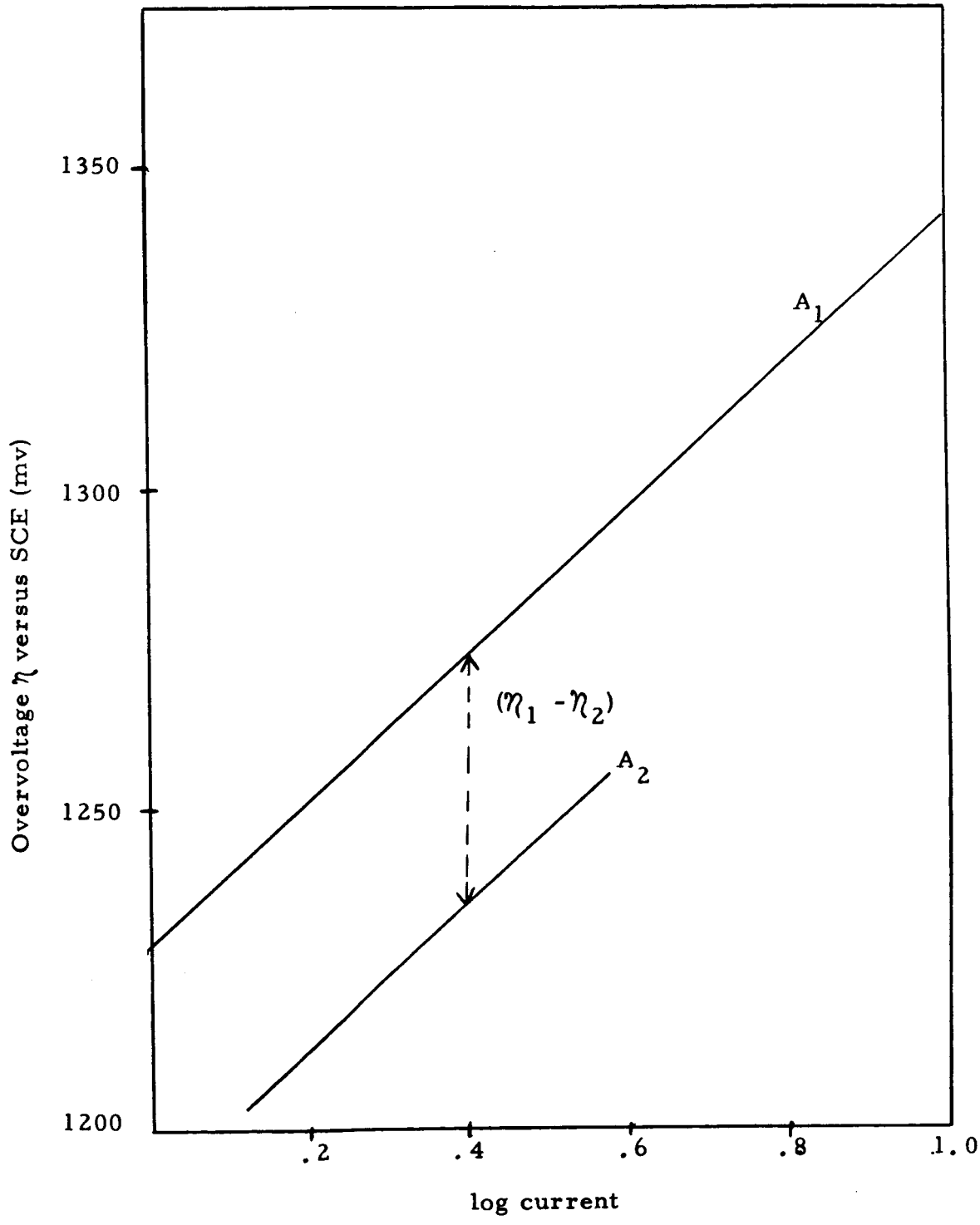

Figure 1. Tafel plots for hydrogen evolution on two nickel cathodes

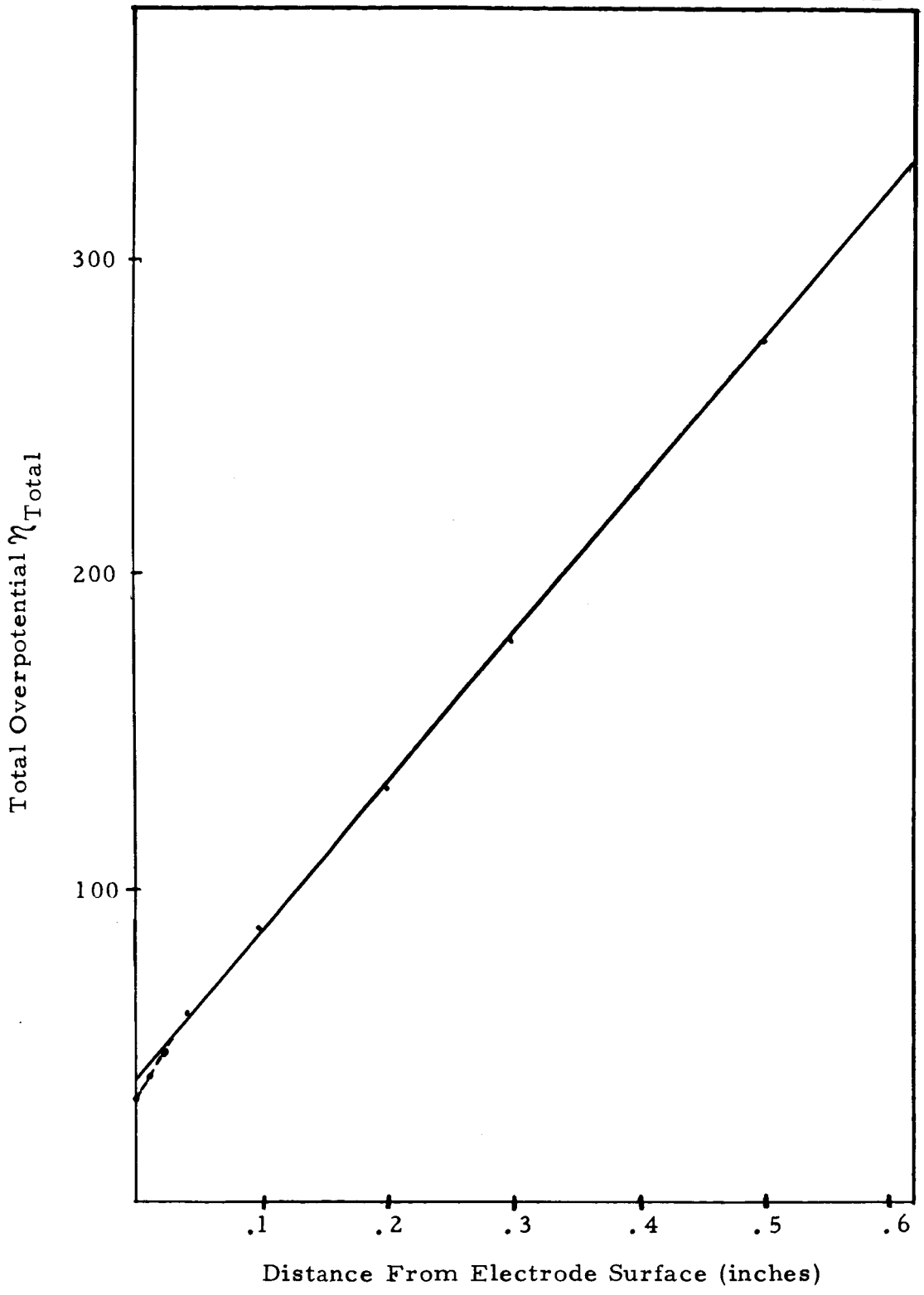

Figure 2. Potential as a function of distance from the electrode surface at 2.00 ma/cm^2

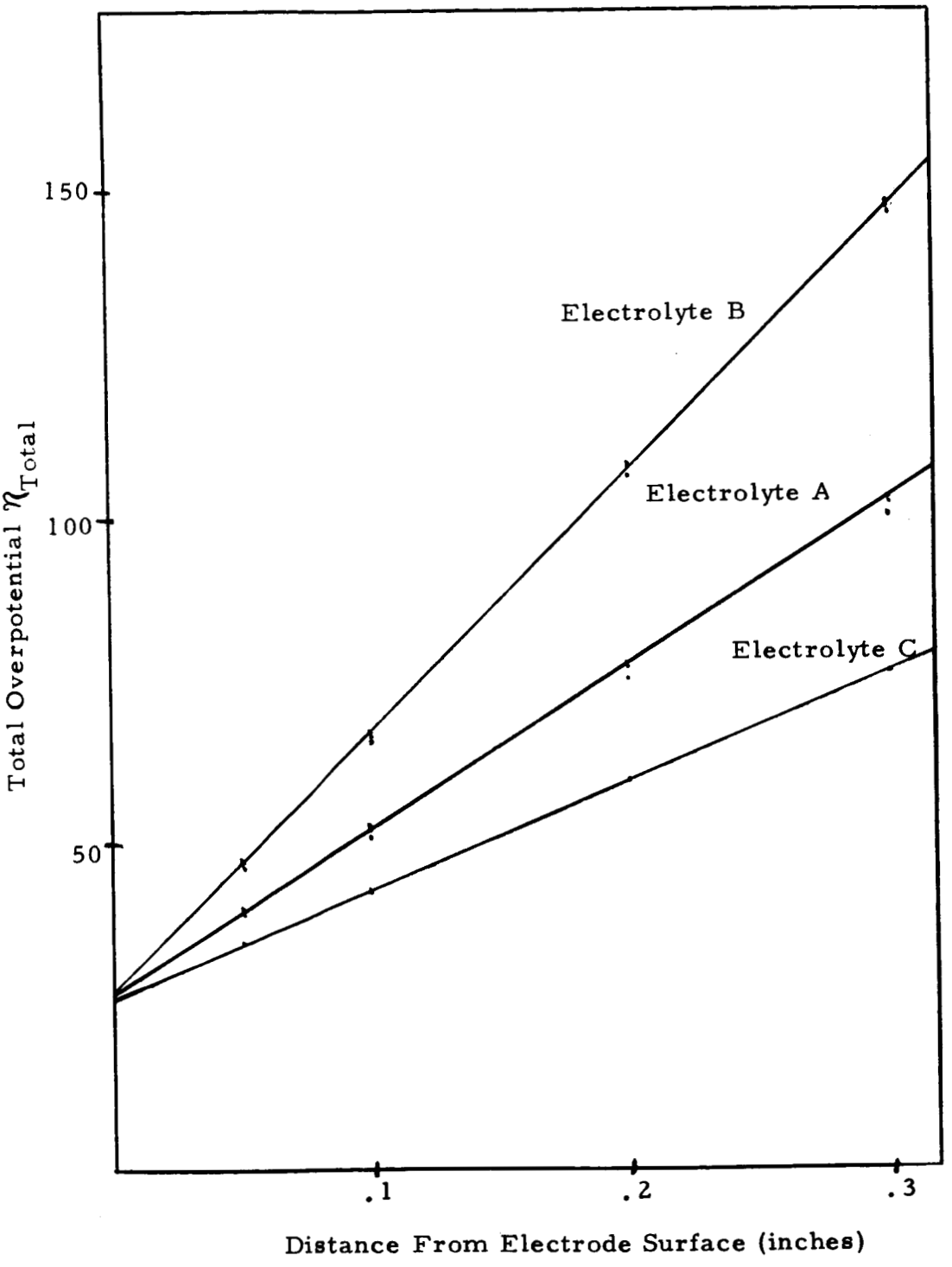

Figure 3. Potential as a function of distance from the electrode surface at 0.96 ma/cm^2. The three plots are for the three electrolytes on page 2

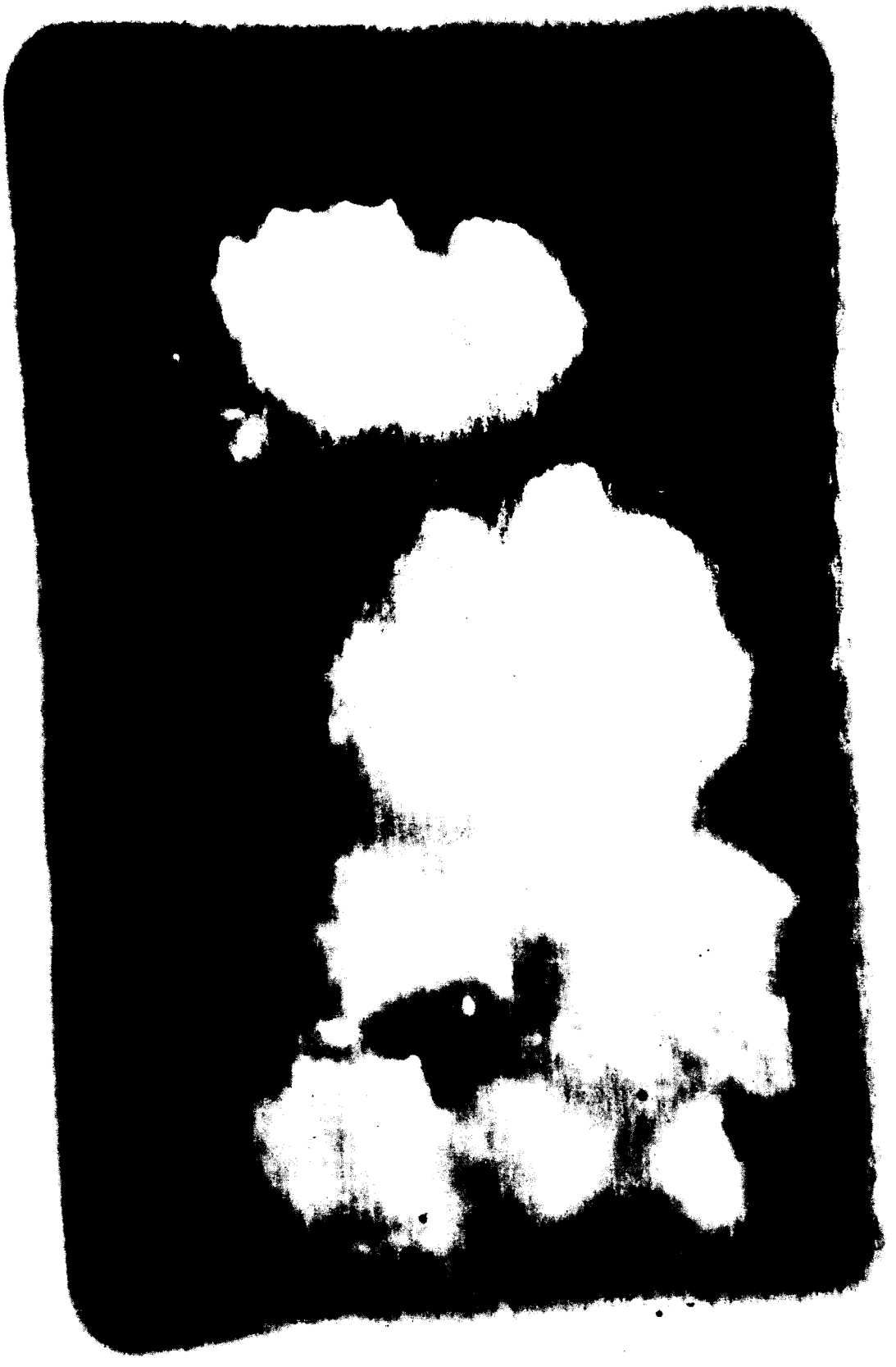

Figure 4. Photomicrograph of silver particle used in control electrode.

REFERENCES

1. E. A. Butler and A. U. Blackham, "Studies of Reaction Geometry in Oxidation and Reduction of the Alkaline Silver Electrode," Final Report, JPL 951554, April 1967.

2. C. Wagner, J. Electrochem. Soc., 98, 116 (1951).

3. Gosta Wranglen and Ake Warg, Acta. Chem. Scand., 15, 1411 (1961).

4. C. W. Tobias, M. Eisenberg, and C. R. Wilke, J. Electrochem. Soc., 99, 359C (1952).

5. H. E. Haring, Trans. Electrochem. Soc., 49, 417 (1926).

6. S. Barnartt, J. Electrochem. Soc., 106, 722 (1959).

7. J. M. Pearson, Trans. Electrochem. Soc., 81, 485 (1942).

8. J. E. Draley and others, J. Electrochem. Soc., 106, 490 (1959).

9. M. Stern and A. L. Geary, ibid., 104, 56 (1957).

10. S. Barnartt, ibid., 108, 102 (1961).

11. J. A. Allen, Trans. Faraday Soc., 48, 273 (1952).

12. M. F. Skalozubov, F. I. Kukoz, and G. V. Mikhailenko, Akad. Nank. SSSR, Otd. Obshchi. i. Tekhn. Khim. Sb. Statei., 1965, 280, C. A. 65:4997e (1966).

13. C. P. Wales and J. Burbank, J. Electrochem. Soc., 106, 885 (1959).

14. N. Cabrera and N. F. Mott, Repts. Progr. in Physics, 12, 163 (1949).